Passion Fruit Seed Oil as Alternative Feedstock for Biodiesel Production via Transesterification

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***Abstract*-The aim of this research was to evaluate potential of passion fruit seeds, an agro-industry byproduct, as a biofuel feedstock. Oil was extracted from the passion fruit seeds, and transesterified to produce biodiesel. KOH was used as a catalyst. The test conditions were; methanol and oil molar ratio between 3:1 to 9:1, catalyst concentration of 1 – 2% w/w at a fixed temperature of 65°C. The reaction time was varied between 5 to 120 min. From the experimental results, maximum biodiesel yield of 93% was obtained at methanol and oil molar ratio of 6.5, catalyst concentration of 1.25%, and reaction time of 60 min. The ester content of biodiesel product was over 96.5%, in accordance with the requirements by Thai and international standards.**

Keywords-alcoholysis; biodiesel; biomass conversion; vegetable oil; renewable energy

I. INTRODUCTION

The Thai government has introduced several strategies to reduce energy consumption and to make use of maximum available indigenous resources in energy supply, among the most promising ones are the energy conservation program, the energy efficiency improvement program, and the renewable energy development program [1-3]. Thailand plans to increase the use of alternative fuels in transport sector where diesel accounts for more than 50% of transport fuel in the country. The national roadmap is to develop raw materials and replace 5% of the total diesel consumption in the transport sector with biodiesel by 2011 and increase to 10% by 2012. It was projected that biodiesel consumption of about 3100 million litres in 2012 will result in savings of foreign exchange of about US$675 million per year [1, 2]. Apart from saving on energy imports, the benefits will also include reduction of fossil fuel consumption and emissions of hydrocarbons, sulfur oxides, carbon and particulate matter. This will make positive impacts on global warming as well as peoples' health.

The most common process used for biodiesel production in Thailand is transesterification of vegetable oils where they are reacted with methanol (methanolysis) to make methyl esters of the straight chain fatty acid. Transesterification reaction proceeds well in the presence of some homogeneous catalysts such as potassium hydroxide (KOH), sodium hydroxide (NaOH) and sulfuric acid, or heterogeneous catalysts such as metal oxides or carbonates [4-8]. Bases can catalyze the reaction by removing a proton from the alcohol, thus making it more reactive, while acids can catalyze the reaction by donating a proton to the carbonyl group, thus making it more reactive. The purpose of the transesterification process is to lower the viscosity of the oil so that it is compatible with current diesel engine systems [9, 10].

At present, more than 95% of the world biodiesel is produced from edible oils which are easily available on large scale from agriculture [11, 12]. However, continuous and large scale production of biodiesel from edible oils has recently been of great concern because they compete directly with food materials – the food versus fuel dispute. Due to tremendous demand for edible oils as food, it is apparent that use of non-edible vegetable oils is very important for developing countries. Production of biodiesel from different non-edible oilseed crops has been extensively investigated over the past several years. Some of these non-edible oilseed crops include jatropha (Jatropha curcas), karanja (Pongamia pinnata), tobacco seed (Nicotiana tabacum L), rice bran, mahua (Madhuca indica), neem (Azadirachta indica), rubber seed (Hevea brasiliensis), and microalgae [12]. The search for potential non-edible oils that can be used for biodiesel production is increasingly intensified.

Passion fruit, a native to Brazil, is a popular tropical fruit throughout the world. The soft, orange pulp of this fruit is full of tiny albuminous seeds (up to 25% of the fresh pulp by weight), and all of these are edible [13, 14]. The passion fruit is usually used for juice production in Taiwan and elsewhere in Asia, and works best as a flavoring additive in many delicacies. In the juice industry, the passion fruit produces many thousand tons of seeds as agricultural byproducts during juice extraction [14]. These seeds, containing large amounts of fiber and oil, are generally discarded after being crushed. In recent years, many studies have aimed to investigate dietary fibers from the byproducts and various fruits with a view to explore their potential applications and physiological activities [15, 16]. To the authors' knowledge, investigation on vegetable oil extracted from passion fruit seeds has not yet been explored.

In this study, potential of passion fruit seed oil as biodiesel feedstock was investigated. The objectives of this research were; (i) to produce biodiesel from passion fruit seed oil, and (ii) to identify its optimum production conditions. The parameters affecting the methyl esters formation are reaction time, molar ratio, catalyst content and reaction temperature.

II. EXPERIMENTAL

After juice extraction, the seeds of passion fruit were collected from the Farmers Association of Mae Hong Son, Thailand. The seeds were cleaned and finely grounded to 0.5 mm in size for analyses. Moisture content was estimated by drying the seed samples at 120°C for 12 h until its weight was constant. The seed powder was fed to screw press. The seed meal was subsequently extracted with petroleum ether. Sample of the oil obtained was sent for analysis for its composition and free fatty acid (FFA) content.

The passion fruit seed oils were transesterified by heating them with a large excess of anhydrous methanol and a catalyst. In this work, alkali catalyzed transesterification method was adopted. KOH was dissolved in methanol by vigorous stirring in a beaker. The oil was transferred into the reactor, then, the catalyst/alcohol mixture was mixed into the oil. The final mixture was heated and stirred vigorously at 65^{o}C in ambient pressure. In this work, methanol to oil molar ratio, catalyst concentration, and reaction time were varied between 3:1 to 9:1, 1.0 to 2.0% w/w, and 5 to 120 min, respectively. A successful transesterification reaction produced two separate liquid phases: ester and crude glycerin. Phase separation was observed within 30 min, but left to complete settling for 24 h. Crude glycerin, the heavier liquid, was collected at the bottom after settling. Water was then added to the methyl ester and stirred for 10 min. Air was also carefully introduced into the aqueous layer while simultaneously stirring very gently. This process was continued until the ester layer became clear. The glycerin was allowed to settle again. The aqueous solution was eventually drained. Washing the ester was performed with water for several times. Subsequently, moisture removal process was carried out by heating the biodiesel product to 105^{o}C in an open container until there was no more steam from the fuel. An advantage of heating was that it drives off any traces of remaining alcohol within the product.

TABLE I. COMPOSITION OF PASSION FRUIT SEED OILS

Fatty acid composition	value (g /100 g)
Myristic acid (C14:0)	0.06
Pentadecanoic acid (C15:0)	0.03
Palmitic acid (C16:0)	10.09
Heptadecanoic acid (C17:0)	0.07
Stearic acid (C18:0)	2.12
Arachidic acid (C20:0)	0.15
Saturated fat	12.52
Palmitoleic acid (C16:1n7)	0.05
cis-10-Heptadecenoic acid (C17:1n7)	0.04
cis-9-Oleic acid (C18:1n9c)	12.68
cis-9,12-Linoleic acid (C18:2n6)	69.79
Œ- Linoleic acid (C18:3n3)	0.13
Mono-unsaturated fatty acid	12.77
Poly-unsaturated fatty acid	69.92
Unsaturated fat	82.69

III. RESULTS AND DISCUSSION

A. Raw Material Properties

The extracted passion fruit seed oils were analyzed for its composition. Screw press was used to obtain oil directly with resulting yields of passion fruit seed oil of around 20% w/w. The composition of seed oil was determined by gas chromatography. Test results are shown in Table 1. The amount of saturate fat and unsaturated fats was found to be 12.52 g/100g and 82.69 g/100g respectively. FFA level of the passion fruit seed oil was found to be approximately 1.44 mg KOH/g.

B. Effect of Molar Ratio on Biodiesel Yield

One of the most important variables affecting the yield of biodiesel is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction forward successfully.

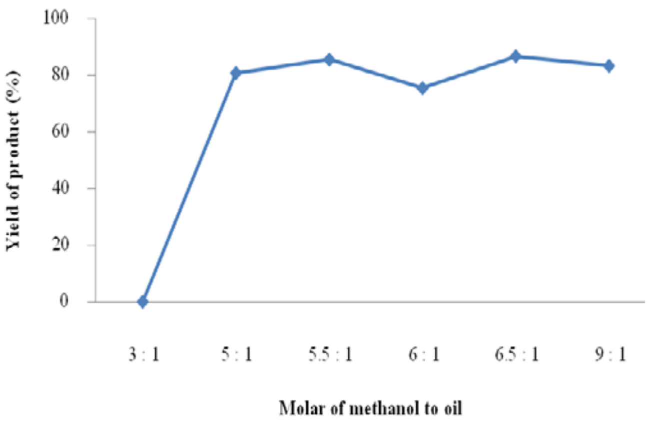

Figure 1. Variation of product yield with methanol to oil molar ratio, KOH concentration = 1.25%, reaction time = 30 min, temperature = 65^{o}C.

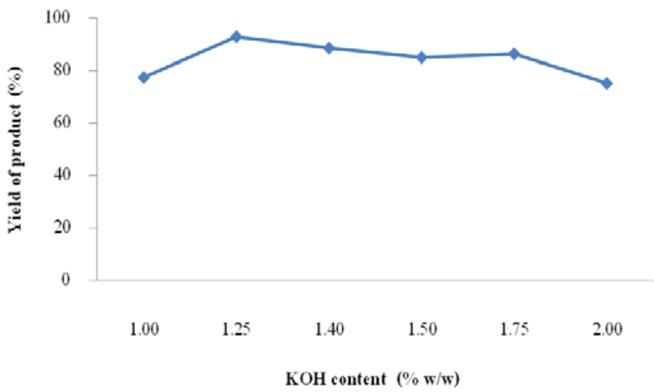

Figure 2. Variation of product yield with catalyst concentration, methanol to oil molar ratio = 6.5:1, reaction time = 30 min, temperature = 65^{o}C.

The transesterification of passion fruit seed oil with methanol was studied at molar ratios between 3:1 and 9:1.

Results are shown in Fig. 1. The yield of biodiesel increased with increasing the molar ratio of alcohol to oil. It can be seen that high conversions of over 70% were obtained for molar ratios between 5:1to 9:1. From the results obtained, it was found that to get maximum conversion of seed oil to biodiesel, a molar ratio of 6.5:1 should be used. However, high alcohol content in high molar ratio of alcohol to passion fruit seed oil can interfere with the separation of glycerin because there was an increase in solubility. When glycerin remained in the product, it can help drive the equilibrium backward, lowering the yield of esters. For molar ratios less than 5:1, the reaction was found to be less complete.

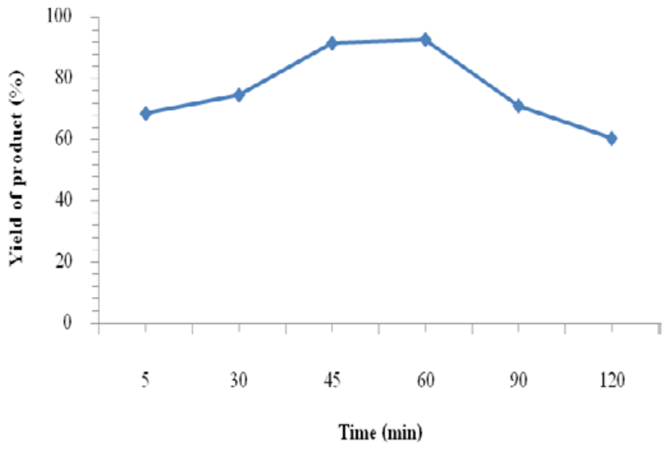

Figure 3. Variation of product yield with reaction time, KOH concentration = 1.25%, methanol to oil molar ratio = 6.5:1, temperature = 65°C.

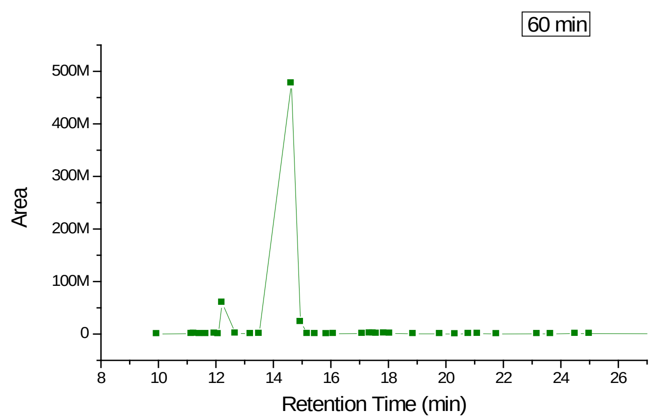

Figure 4. GC/MS chromatogram of biodiesel from passion fruit seed oil.

C. Effect of Catalyst Concentartion on Biodiesel Yield

Biodiesel yields as a function of KOH catalyst concentrations between 1.0 to 2.0% w/w of the seed oil are shown in Fig. 2, for a fixed methanol to oil molar ratio of 6.5:1. High conversions above 70% were obtained for all cases. At 1.25% KOH concentration, maximum yield of over 90% was realized.

D. Effect of Reaction Time on Biodiesel Yield

Passion fruit seed oil was transesterified at different times under the fixed condition of methanol–oil molar ratio 6.5:1, 1.25% KOH catalyst and 65°C. Yields of at least 60% were obtained, shown in Fig. 3. It is known that conversion rate increases with reaction time. In this work, the expected trend was observed for up to 60 min, after which a decline in yield was obtained. High product yields of 91.6 and 92.8% were obtained at 45 and 60 min, respectively.

E. Biodiesel Composition

In this work, limited numbers of biodiesel samples were sent for analysis by GC-MS. Carbon cleaved peaks of compounds obtained from passion fruit seed oil such as hydrocarbon, aldehyde, alcohol and acid were detected and plotted during the first 25 minutes of the chromatogram. Result is depicted in Fig. 4. The triacylglycerols are esters of long chain carboxylic acids combined with glycerol. Carboxylic acids R–C-(O)–O–H can be converted to methyl esters R–C-(O)–O–CH_3 by the action of a transesterification agent. It was found that the biodiesel product consisted of various kinds of fatty acid methyl esters. High relative contents of 8,11-octadecadienoic acid and hexadecanoic acid were observed. Its ester content was found to be over 96.5%, in accord with the requirements by the national standards.

By analyzing the components of biodiesel, it was found that biodiesel product consisted of various kinds of fatty acid methyl esters, among which relative contents of palmitic acid methyl esters and linolenic acid methyl esters were high. Glycerol was obtained as a by-product after transesterification. Compared with diesel oil, main properties of biodiesel were shown to be similar to that of the mineral diesel oil.

IV. CONCLUSION

As an alternative fuel, passion fruit seed oil has a potential to be used as bioenergy feedstock. The optimum condition was methanol and passion fruit seed oil of 6.5:1, using KOH of 1.25% w/w, and the reacting period of 60 min, obtaining the maximum biodiesel yield of around 93% with ester content of over 96.5%. Biodiesel from passion fruit seed oil can play an important role in meeting future fuel requirements.

ACKNOWLEDGMENT

The authors would like to thank the Graduate School, Chiang Mai University, and the Commission of Vocational Education for supports.

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